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Bipolar charge transport property of *N*,*N*′-dicarbazolyl-1,4-dimethene-benzene: A study of the short range order model

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Short range order model is commonly used to explain the charge transport property of disordered organic semiconductors. However, its validity is not yet studied. In this paper, the hole and electron mobilities of a bipolar material, *N*,*N*′-dicarbazolyl-1,4-dimethene-benzene (DCB), were measured through time of flight method. The hole and electron mobilities of DCB based on the crystalline structure were calculated. In order to investigate the short range order model, the ratios of charge mobilities at zero electric field of holes to electrons were calculated. The results showed that this model cannot fully explain our case. The reason was discussed in detail, and a correction method was proposed. We showed that using the short range order model without preconditions to explain the charge transport property of amorphous materials may lead to deviations, which is often neglected in the past.

charge transport, short range order, DCB, carrier mobility

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Organic amorphous semiconductors were widely applied in devices like organic light emitting diodes (OLEDs), organic thin film transistors (OTFTs) and organic solar cells (OSCs). Charge transport mobility is one of the most important properties for organic semiconductors to improve device performance and is of much interest ever since. While different techniques to measure the charge mobility in organic semiconductors have already been developed, ways to evaluate the charge mobility theoretically are still being explored. For crystalline materials, some effective ways have already been developed [1]. Charge mobility of an amorphous organic semiconductor, on the other hand, is difficult to predict due to its complicated intermolecular arrangement. Instead of directly calculating the charge mobility in adisordered organic semiconductor, another method is often used to estimate the charge transport properties: a method using short range order model where the intermolecular arrangement in a disordered organic semiconductors is assumed to be similar to the arrangement in the crystalline structure [2,3]. Therefore one can perform calculations based on the crystalline structure to explain the charge transport properties of amorphous films [4–6]. In the short range order model which is used to determine whether a specimen is a hole transporting material or an electron transporting material, one assumes that the ratio of hole zero-field mobility to the electron zero-field mobility in amorphous film is close to that in crystals [2,4,5]. More precisely, the ratio of the mobility at zero electric field of holes to that of electrons determines whether a material is hole transporting, electron transporting or bipolar. Unlike anisotropic molecular distribution in crystal, however, amorphous material is isotropic. Therefore the short range order model is expected to lead to disagreement with the experimental results.

N,*N*′-dicarbazolyl-1,4-dimethene-benzene (DCB) is a high-efficiency blue phosphorescent host material [7,8]. In this

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paper, conventional time-of-flight (TOF) method was used to measure the hole and electron mobilities of the vacuum deposited films of DCB. Through the calculation of reorganization energies and charge transfer integrals, the hole and electron mobilities of DCB were calculated based on its crystalline structure. To study the short range order model in our system, the value of the charge mobilities in zero electric field, $\mu(0)$, of holes and electrons were deduced, and the ratios of the $\mu(0)$ of holes to that of electrons were calculated both for calculation and experimental results. The validity of the short range order model is studied.

1 Experimental

The DCB film was fabricated through vacuum deposition technology in a vacuum of around 8×10^{-4} Pa. The configuration of the measurement sample is ITO/DCB (1.0 μm)/Ag (100 nm), where ITO is cleaned by ultrasonication in ethanol-acetone (1∶1) and de-ionized water. The deposition rates of organic materials and Ag were 0.2–0.3 and 0.03 nm s^{-1}, respectively. The mobility values were calculated from the transit times, τ, obtained in TOF experiments via the conventional relationship, $\mu=d^2/\tau E$, where d is the film thickness and E is the applied voltage.

2 Computational methods

Within the hopping description, the charge transport can be characterized by a diffusion process [1,9]. In the absence of electric field, the charge mobility $\mu(0)$, can be expressed as the Einstein-Smoluchowski relation [1,9,10]:

$$\mu(0)=\frac{eD}{k_BT}, \tag{1}$$

where e is the elemental charge, D is the diffusion coefficient, k_B is the Boltzmann constant and T is the temperature.

For a spatially isotropic system, the homogeneous diffusion constant D can be approximately expressed as [1,10–12]

$$D=\frac{1}{2n}\sum_i r_i^2 k_i P_i, \tag{2}$$

where n is the dimensionality, r_i is the distance to neighbor i, k_i is the hopping rate and P_i is the hopping probability which is expressed as

$$P_i=\frac{k_i}{\sum_i k_i}. \tag{3}$$

Therefore, if k_i is known, $\mu(0)$ can be calculated according to eqs. (1)–(3).

Organic semiconductors are considered to have with weak intermolecular interactions and a hopping mechanism [13–15] is often used to describe the charge transport process: holes or electrons hop from a charged molecule to an adjacent neutral molecule. The rate of this charge transfer process, k, can be described by the classic Marcus equation as [16]

$$k=\frac{4\pi^2}{h}V^2\frac{\exp\left(-\lambda/4k_BT\right)}{\sqrt{4\pi\lambda k_BT}}, \tag{4}$$

where λ is the reorganization energy, V is the charge transfer integral between the two adjacent molecules, h is the Plank constant and T is the temperature.

The reorganization energy can be separated into the internal reorganization energy and the external reorganization energy. In most cases, the latter, which is related to the polarization of the surrounding medium, is considered to be small [17] and its contribution to the total reorganization energy can be neglected [4]. Using this approximation, reorganization energy is calculated using the method describing in ref. [9]. The optimization of the molecular structures of DCB in its neutral, cationic and anionic states were performed at B3LYP/6-31G(d) level using Gaussian 03 package [18].

The charge transfer integral, also referred as electronic coupling, is often defined as $<\Psi_1|H|\Psi_2>$, where H is the electronic Hamiltonian of the system and Ψ_1 and Ψ_2 are the wavefunctions of two charge localized states (diabatic states) [9]. The charge transfer integral can be calculated using the site energy correction method [1,10,19–23], and is expressed as [11,22,24–26]

$$V=\frac{h_{12}-\frac{1}{2}\left(h_{11}+h_{22}\right)S_{12}}{1-S_{12}}, \tag{5}$$

$$h_{ij}=\left\langle\Psi_i\middle|H\middle|\Psi_j\right\rangle, \tag{6}$$

$$S_{12}=\left\langle\Psi_1\middle|\Psi_2\right\rangle, \tag{7}$$

where V is the charge transfer integral, S_{12} is the spacial overlap, Ψ_1 and Ψ_2 are the HOMO (for holes) or LUMO (for electrons) molecular orbital of the two isolated molecule, H is the Kohn-Sham Halmiltonian of the dimer system.

The calculation of monomers and dimers of different pathways were calculated at PW91PW91/6-31+G(d) level using Gaussian 03 package [18] and a counterpoise basis set is applied [26].

3 Results and discussion

Figure 1 shows the molecular structure of DCB. The hole and electron mobilities at different electric fields measured

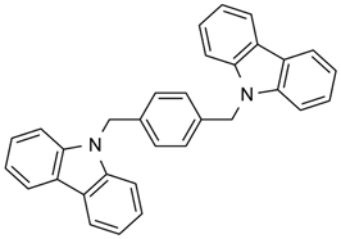

Figure 1 Chemical structure of DCB.

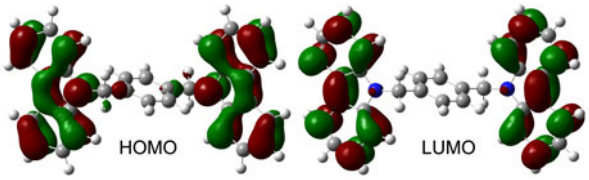

Figure 3 (Color online) Isocontour plots of HOMO and LUMO wavefunctions for DCB obtained at the RB3LYP/6-31G(d) level. All the MO surfaces correspond to an isocontour value of $|\Psi|$=0.025 a.u.

from TOF experiments are showen in Figure 2. Charge mobilities calculations would be performed on the assumption that no external electric field is applied, so that the charge mobilities at zero electric field, $\mu(0)$, must be obtained to compare experimental and theoretical results. Organic semiconductors commonly obey the Poole-Frenkel behavior over the range of electric fields of 10^4–10^5 V cm^{-1} [9]. But this behavior is also observed in many cases at lower electric fields [9]. Hence $\mu(0)$ was deduced by extending the mobility vs electric field intensity curves to zero electric field, and the values of $\mu_h(0)$ (hole mobility at zero electric field) and $\mu_e(0)$ (electron mobility at zero electric field) for DCB are 4.05×10^{-6} and 5.15×10^{-7} cm^2 V^{-1} s^{-1}, respectively. The hole mobility of DCB is one order of magnitude higher than its electron mobility, suggesting it is a bipolar transport material.

The hole and electron reorganization energies were calculated to be 0.070 and 0.138 eV, respectively. Figure 3 shows the HOMO and LUMO wavefunctions of DCB.

The space group of DCB is *P*21/*c* and there are two molecules in one unit cell [27]. One molecule in a unit cell can be obtained through symmetry operation from the other molecule, therefore studying one kind of molecule can go through all possible transport pathways. We chose the molecule the center of mass of which is at (0,0,0) as the target and used it to form possible transport pathways with its surrounding molecules. The calculation results of charge transfer integrals are shown in Table 1. As we can see, the hole and electron transfer integrals of the pathway at the direction (1,0,1) are significantly higher than those of all the other pathways. The molecular structure of this special pathway is shown in Figure 4. And we will further discuss this issue later.

According to eqs. (1)–(3), hole and electron mobilities were calculated to be 2.98 and 5.66 cm^2 V^{-1} s^{-1}, respectively,

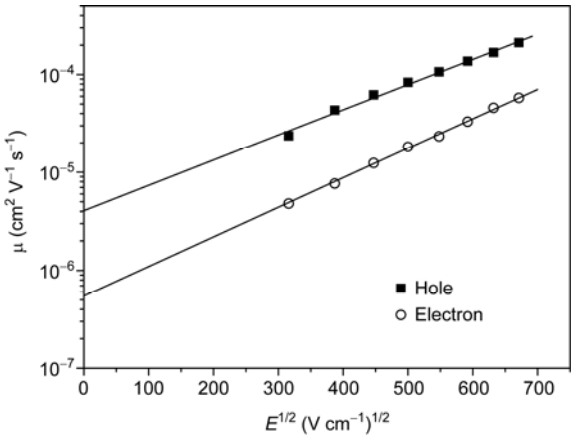

Figure 2 The hole and electron mobilities of DCB amorphous film at different film.

Table 1 Charge transfer integral calculation results

Direction[a)]	r_i [b)] (Å)	V_h [c)] (meV)	V_e [d)] (meV)
(1,0,0)	14.00	17.12	3.69
(0,1,0)	9.45	1.00	–0.22
(0,0,1)	9.45	3.77	11.11
(0,1,–1)	16.89	0.02	–0.07
(0,1,1)	16.89	–0.23	0.00
(1,0,–1)	14.36	–0.03	–0.01
(1,0,1)	11.16	37.71	78.80
(–1,1,0)	16.50	0.02	–0.10
(1,1,0)	16.50	–0.76	–0.05
(–1,1,–1)	17.91	–0.49	–0.60
(–1,1,1)	20.05	0.33	–0.01
(1,1,–1)	20.05	0.65	0.00
(1,1,1)	17.91	0.15	0.00
(2,0,0)	8.72	–1.47	0.07
(2,0,1)	17.67	–0.51	3.17
(0,0.5,–0.5)	8.45	–5.23	9.00
(0,0.5,0.5)	8.45	–4.10	8.25
(0,0.5,–1.5)	15.81	0.29	–0.04
(0,0.5,1.5)	15.81	–0.25	–0.08
(–1,0.5,–0.5)	11.27	–5.62	2.14
(–1,0.5,0.5)	12.95	0.09	–3.78
(1,0.5,–0.5)	12.95	–0.59	1.16
(1,0.5,0.5)	11.27	–2.73	–1.56
(–1,0.5,–1.5)	16.28	–0.66	0.99
(1,0.5,1.5)	16.28	0.39	0.90

a) The coordinates of the mass center of the second molecule in a pathway; b) the distance between the mass centers of two molecules; c) hole transfer integral; d) electron transfer integral.

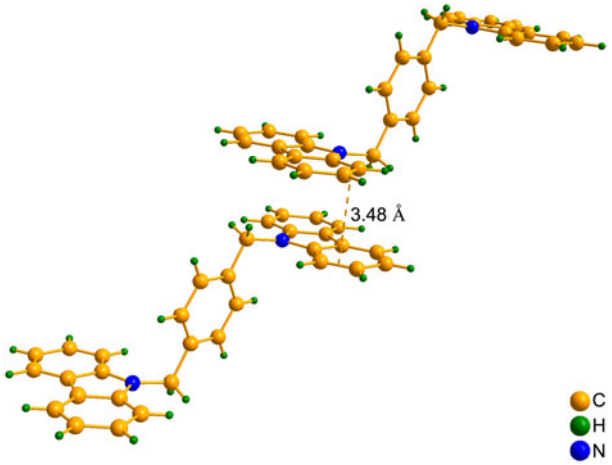

Figure 4 (Color online) The molecular structure of the pathway at the direction (1,0,1).

as shown in Table 2. If the short range order model is applied here, the $\mu_h(0)/\mu_e(0)$ value obtained from the measurement of amorphous films and that of the calculations based on the crystalline structure should be close. However, the results showed that $\mu_h(0)/\mu_e(0)$ values were calculated to be 7.86 and 0.53 for experimental measurement and theoretical calculations, respectively, as shown in Table 2. These values are widely deviated from the measured zero-field mobilities. In other words, $\mu_h(0)/\mu_e(0)$ value from amorphous films measurement is 14.8 times as large as that obtained from crystalline structure calculation. This suggests that the short range order model is not appropriate here. We will explain the results as follows.

As seen in Figure 2, the $\log\mu$ versus $E^{1/2}$ curve for holes and electrons are nearly parallel, which means that the influence of electric field on hole transport and electron transport are similar. Therefore it is rational to conclude that at a very small electric field, even if the $\log\mu$ versus $E^{1/2}$ curve is not liner, the influences of electric field on hole mobility and electron mobility are still close. In other words, the finite electric field did not have much influence on the deduced hole versus electron mobility values. Therefore the hole versus electron mobilities at zero electric field deduced from finite electric fields should be close to "the real zero electric field" case. There is no need to worry that different charge transport paths are caused by finite electric field.

Eqs. (1)–(4) represent the basic idea to calculate the charge mobilities based on the crystalline structure. It can be concluded that pathways with relative high charge transfer integral are more important in charge transport. Paticularly, if one charge transport pathway possesses extremely high charge transfer integral compared to all other pathways, it will dominate charge transport and the calculated charge mobility is more of the charge transport property of this particular pathway. This makes sense in crystals for their anisotropic properties. However, it will make the short range order model invalid. Because under such circumstances, applying the short range order model actually becomes to explain the charge transport properties of amorphous films using one particular charge transport pathway in crystalline structure, which is clearly not appropriate.

We have already noticed there is a special transport pathway (Figure 4) the hole and electron transfer values of which are significantly larger than all the other pathways. Apart from this pathway, the highest hole and electron transfer integrals are 17.12 and 11.11 meV, respectively. Such a special pathway which dominates charge transport in crystalline structure cannot stand for the situation in amorphous materials. And its existence makes the short range order model invalid. However, if this pathway is excluded, the "one pathway dominance" situation will end, so that short range order model may become valid again. Then we applied this correction, and the new hole and electron mobilities were calculated to be 3.58×10^{-1} and 5.38×10^{-2} $cm^2\ V^{-1}\ s^{-1}$, respectively, as shown in Table 2. The new $\mu_h(0)/\mu_e(0)$ value is 6.65, which is very close to the measured value of 7.86. This result proves that our analysis is right.

Both the corrected hole and electron mobilities are 5 orders of magnitude higher than those obtained from experiment. It must be pointed out that performing more complicated calculations which yield mobility values closer to experimental results is not our goal. Calculations are based on crystalline structure, and defects were not taken into account. Therefore it is rational that the calculated mobilities are much higher than the experimental values. Additionally, this would not have much influence because the short range order model is about the hole versus electron mobility.

It is convenient to use the short range order model to preestimate or understand the charge transport properties of organic amorphous materials. However, despite its idea of simplicity, this model cannot be used unconditionally. Under special conditions, additional attention must be paid in order to get a precise result. In our case, removing a dominating carrier transport pathway to make the environment in crystalline structure more similar to the situation in disordered materials.

Table 2 Charge mobilities obtained though experiment and calculation

	$\mu_h(0)$ ($cm^2\ V^{-1}\ s^{-1}$)	$\mu_e(0)$ ($cm^2\ V^{-1}\ s^{-1}$)	$\mu_h(0)/\mu_e(0)$
Measured value	4.05×10^{-6}	5.15×10^{-7}	7.86
Calculated value	2.98	5.66	0.53
Corrected calculated value	3.58×10^{-1}	5.38×10^{-2}	6.65

4 Conclusion

Hole and electron mobilities in DCB disordered film were measured through TOF method and charge mobilities at zero electric field were deduced. Hole and electron mobilities of DCB were calculated based on the crystalline struc-

ture. $\mu_h(0)/\mu_e(0)$ values of the amorphous film and the crystalline structure were calculated, and the validity of the short range order model was studied. There is one unique charge transport pathway, which is very different from all the other pathways and dominates charge transfer in crystalline structure. We considered that such a unique pathway should not exist in amorphous films in which the intermolecular arrangement is isotropic and disordered. The measured and calculated results are in good accordance with each other after correction.

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